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An Examination of Glass-fiber and Epoxy Interface Degradation in Printed Circuit Boards

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Abstract

Conductive filament formation or CAF typically occurs in two steps: degradation of the resin/glass fiber bond followed by an electrochemical reaction. Bond degradation provides a path along which electro-deposition occurs due to electrochemical reaction. The path results from poor glass treatment, from the hydrolysis of the silane glass finish, or from mechanical stresses. Once a path is formed, an aqueous layer can develop through the adsorption, absorption, and capillary action of moisture at the resin/fiber interface. The path can be modeled as an electrochemical cell, in which the metal conductors are the electrodes, the driving potential for the electrochemistry is the operating potential of the circuit, and the electrolyte is the absorbed moisture.

Microscopic examinations of failure sites have shown that conductive filaments can be formed along debonded or delaminated fiber glass/epoxy resin interfaces due to breaking of the organosilane bonds. The organosilane bonds can be chemically degraded by hydrolysis (adsorption of water at the fiber glass/epoxy resin interface) or by repeated thermal cycling, which induces stresses at the interface due to coefficient of thermal expansion mismatches. This paper discusses the formation of pathways due to the degradation of organosilanes.

Introduction

Multi-layer organic laminates, which make up over 90% of the interconnecting substrates in electronics (standard FR-4 represents 85% of the substrates used for laminates), can develop a loss of electrical insulation resistance between two biased conductors due to conductive filament formation. The probability of conductive filament formation is a function of the temperature, moisture content, voltage bias, manufacturing quality and processes, materials, and other environmental conditions and physical factors.

With increases in design density and tighter spacing between conductors, the probability of failure due to conductive filament formation (CFF) in printed circuit board (PCB) electronic assemblies has increased. CFF is a failure observed within glass- reinforced epoxy PCB laminates that is caused by an electrochemical process involving the ionic transport of a metal through or across a non-metallic medium under the influence of an applied electric field [1] [2]. The growth of the metallic filament is a function of temperature, humidity, voltage, laminate materials, manufacturing processes, and the geometry and spacing of the conductors [2]. The growth of these filaments can cause an abrupt loss of insulation resistance between the conductors under a DC voltage bias.

A statistical examination of field returns and root cause analysis performed at Center for Advanced Life Cycle Engineering at University of Maryland shows that failures in PCBs account for a significant percentage of field returns in electronic products and systems. Studies on CFF [2] [3] have found that path formation in a PCB is often along the glass fiber to epoxy matrix interface, as shown in Figure 1 .

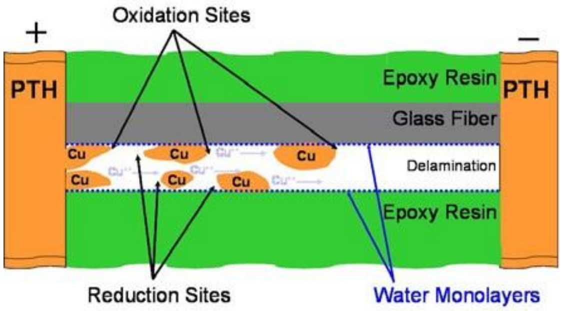

Figure 1 Schematic describing CFF growth [3]

Delamination along the fiber/resin interface can occur as a result of stresses generated under thermal cycling due to coefficient of thermal expansion (CTE) mismatch between the glass fiber (CTE~5.5 ppm/°C) and the epoxy resin (CTE~65 ppm/°C) (Figure 2). CFF can take place in the plated-through-hole to plated-through-hole (PTH- PTH), PTH-plane, and trace-trace geometries.

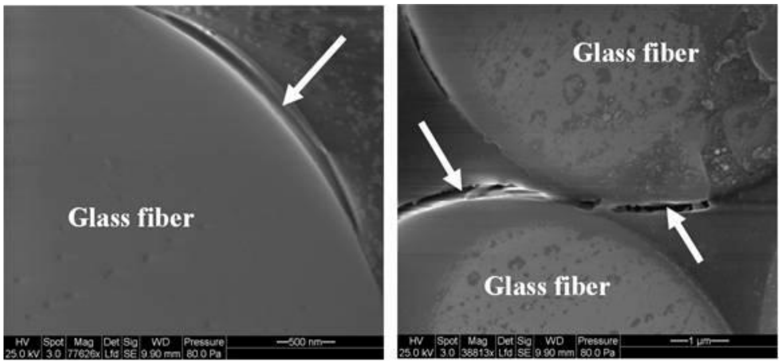

Figure 2 CFF growth path along the glass fiber and resin interface [3]

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A two-step model was developed to explain the growth of conductive filaments at the resin-glass interface in PCBs [1][3], where degradation of the resin-glass interfacial bond first occurs, followed by an electrochemical reaction. According to Lando [2], the path required for the transportation of metal ions formed by the degradation of the resin- glass interfacial bond results from mechanical release of stresses, poor glass treatment, hydrolysis of the silane glass finish, or stresses originating from moisture-induced swelling of the epoxy resin. Path formation was reported to be independent of bias; however, humidity was identified as a contributing factor towards degradation. After path formation, the PCB is viewed as an electrochemical cell. In this cell, the copper conductors are the electrodes, the absorbed water is the electrolyte, and the driving potential for the electrochemistry is the operating or test potential of the circuit. The electrode reactions for the metal migration are:

At the anode:

$$Cu \rightarrow Cu^{n+} + ne^- \qquad 1$$

$$H_2O \rightarrow \frac{1}{2}O_2 \uparrow + 2H^+ + 2e^- \qquad 2$$

At the cathode:

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 \uparrow + 2OH^- \qquad 3$$

Pathway Formation in CFF

In printed circuit boards, one manner in which pathway between conductors is formed is chemical hydrolysis of the silane glass finish or coupling agent. Past work has shown that the glass epoxy interface absorbs 5 to 7 times more moisture than the bulk epoxy [5]. A common cross-linking agent used in FR-4 and many other epoxy-based laminated systems is dicyandiamide (aka dicy). Dicy and glass surface are both hydrophilic. This combination of a hydrophilic surface and a hydrophilic cross-linking agent is one of the factors responsible for degradation of the glass fiber/epoxy resin interface due to hydrolysis. Williams [6] has shown that PCBs manufactured with non- dicy cross-linked epoxy resins are more resistance to CFF failures than PCBs manufactured with dicy cross-linked epoxy resins.

Organosilanes are bifunctional molecules that act as adhesion promoters, crosslink agents, and moisture scavengers in adhesive and sealant products [7]. Silane adhesion promoters act as molecular bridges between two chemically different materials and have been shown to dramatically improve the adhesion of polymeric resins to substrates such as glass, silica, alumina, or active metals.

Figure 3 illustrates a typical alkoxysilane coupling agent and its hydrolysis reaction. Typically, the silane is functional at both ends. R is an active chemical group, such as amino (NH_2), mercapto (SH), or isocyanato (NCO). This functionality reacts with functional groups in an industrial resin or bio molecule such as DNA fragments. The other end consists of a halo (most often chloro) or alkoxy (most often methoxy or ethoxy) silane. This functionality is converted to active groups on hydrolysis called silanols. The silanols can further react with themselves, generating oligomeric variations. All silanol variations can react with active surfaces that contain hydroxyl (OH) groups.

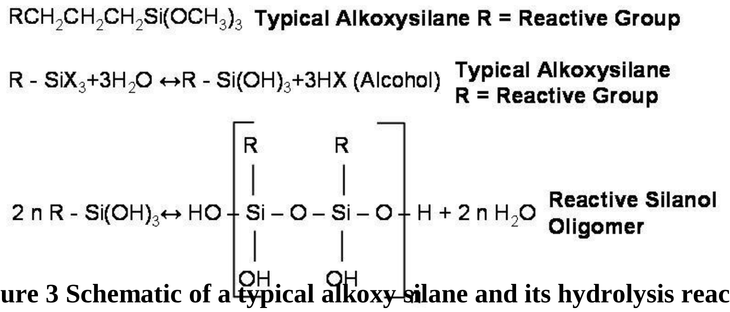

Figure 3 Schematic of a typical alkoxy silane and its hydrolysis reaction

The three main classes of silanes are chloro-, methoxy- and ethoxy- silanes. Chlorosilanes are the most reactive, but evolve corrosive hydrogen chloride on hydrolysis; methoxy silanes are of intermediate reactivity; ethoxy silanes are least reactive and evolve non-toxic ethanol [8]. The difference in reactivity between methoxy and ethoxy silanes is low; at typical hydrolysis pH (acidic ~5, basic ~ 9), both versions hydrolyze in under 15 minutes at 2% silane concentrations.
The bifunctional silane molecules act as a link between the glass fiber and resin by forming a chemical bond with the glass surface through a siloxane bridge, and the organofunctional group bonds to the polymeric resin [9]. This allows silanes to function as surface-treating or "coupling" agents. The formation of an interpenetrating network (IPN) through interdiffusion is the next step in the process. Figure 4 shows a schematic for interdiffusion and creation of an IPN in a silane-treated glass fiber [10]. Interdiffusion and intermixing take place in the coupling agent-polymer resin interface region, due to penetration of resin into the chemisorbed silane layer and migration of the physicsorbed silane molecules into the resin phase. The migration and intermixing of silane and other sizing ingredients with polymer resin create an interphase of substantial thickness.

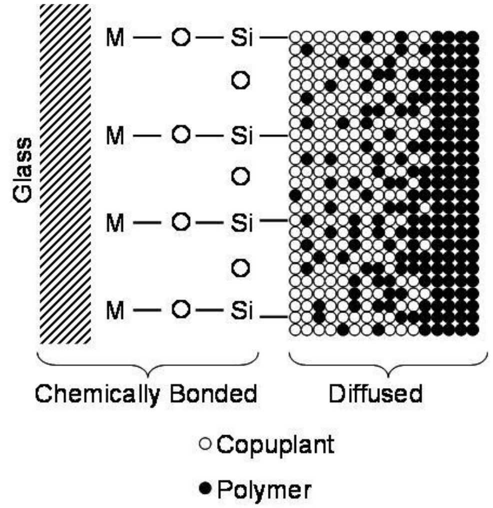

Figure 4 Schematic for conventional interdiffusion and IPN [10]

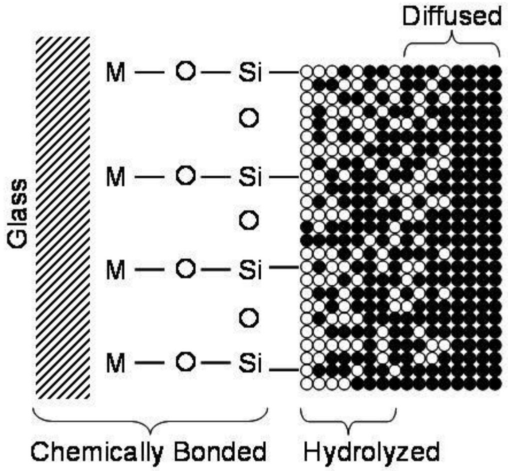

Figure 5 Schematic for hydrolyzed diffused interface after aging in water in a silane treated glass fiber [11]

Theoretically, a single layer of silane may be sufficient to bond with the glass surface; however, to ensure uniform coverage, more than one layer of silane is usually applied. This results in a tight siloxane polymeric network close to the inorganic surface that diffuses into subsequent overlays. The siloxane remain in high concentration at the glass-epoxy interface and may be dissolved into the matrix during curing of the matrix resin, as shown in Figure 5. Coupling to the organic matrix is a complex phenomenon. The reactivity of a thermoset polymer is matched to its reactivity with the silane. For example, an epoxysilane or aminosilane will bond to an epoxy resin; an aminosilane will bond to a phenolic resin; and a methacrylate silane will bond through styrene crosslinking to an unsaturated polyester resin. The large differences in composition and chemical characteristics of the individual components, such as antistats on the glass, lubricants, surfactants, and film formers, further complicate the formation of this interphase with different formulations. While the silane chemistry and its interactions with the glass surface and the polymer have been extensively studied, relatively little information is available about the influence of these sizing components on the formation of the interphase. The interphase is the region where stress transfer occurs between the two composite constituents, but its material properties and effective thickness are unknown. Investigation of the mechanical properties of the interphase presents a challenge to probing into materials in extremely low dimensions.

The silicon atoms in the silanes are bonded to the silicon atoms in the glass through oxygen atoms, the silicon atoms in the glass are bonded to each other. If the water produced in the forward reaction is continuously removed, by evaporation for instance, the bonding of silane to glass will continue until either there is no more silane or no more attachment sites on the glass surface.

Conversely, if water is added to the silane bonded to glass, the reverse reaction can debond the silane from the glass. The rate of hydrolysis is influenced by the pH.

For pathway formation in CAF, the degradation reaction is a second hydrolysis of silane bonds, typically observed after long-term exposure to elevated temperature/humidity conditions. Hydro-thermal degradation of silane bonds in glass/epoxy composites [10][12][14] enables the path formation due to hydrolysis, which is the rate-limiting step in printed circuit board failure due to CFF. The hydrolysis degradation reaction of the interfacial bonds formed with silane coupling agents is shown in equation 4.

$$Si-O-M+H_2O \leftrightarrow Si-O-H+H-O-M \qquad 4$$

where M is the substrate. The rate of degradation is shown in equation 5.

$$-\frac{dC_s}{dt}=k_f f_w C_w f_s C_s \qquad 5$$

where k_f is an elementary rate constant given by equation 6.

$$k_f=\frac{kT}{h} f_w C_w \exp\left(-\frac{\Delta G_O^* + P\Delta V^*}{RT}\right) \qquad 6$$

where k is the Boltzmann constant, h is the Planck constant, R is the gas constant, T is the absolute temperature, f_W is the activity coefficient of the attacking chemical, f_B is the activity coefficient of the interfacial bond, C_W is the concentration of the attacking chemical, C_B is the concentration of the interfacial bond, ΔG_0^* is the change of Gibbs free energy of the activated state, P is the pressure, and ΔV^* is the activated volume per mole [8].

Conclusions

The two step process of conductive filament formation includes the resin/glass fiber bond degradation and pathway formation, followed by an electrochemical reaction between the conductors. One method by which the pathway forms is due to breakage of the organosilane bonds at the glass and resin interface. This breakage occurs by hydrolysis (adsorption of water at the fiber glass/epoxy resin interface) or by repeated thermal cycling, which induces stresses at the interface due to coefficient of thermal expansion mismatches. This paper reviews the organosilane-resin bonding process and summarizes processing and environmental phenomenon that can result in breakage of the bonds. The paper also motivates the requirement for systematic investigation of mechanical properties at the glass/resin interphase, and to track the influences of physio- chemical stresses such as moisture and pH that can affect the strength of this vital interface.

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